Journal of Organometallic Chemistry, 342 (1988) 129–136
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Stoichiometric hydrogenation of α,β-unsaturated ketones by $HCo(CO)_4$

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(Received May 29th, 1987)

Abstract

A study of the kinetics of the stoichiometric hydrogenation of α,β-unsaturated ketones by $HCo(CO)_4$ led to the rate expression rate = k_{obs}[ketone]$[HCo(CO)_4]^2$-$[CO]^{-1}$.

The reaction is catalyzed by $Co_2(CO)_8$ and shows a small inverse isotope effect with $DCo(CO)_4$. Although the analogous reaction with the α,β-unsaturated ester dimethyl α-methylidenesuccinate (dimethyl itaconate, DMI) is also catalyzed by $Co_2(CO)_8$ and also shows an inverse isotope effect, the rate expression involves a first order dependence on $HCo(CO)_4$. Furthermore, contrary to the behavior of simple acrylates, which have been shown elsewhere to conform to the same kinetic expression, no aldehydic product is produced. A mechanism consistent with the results is proposed.

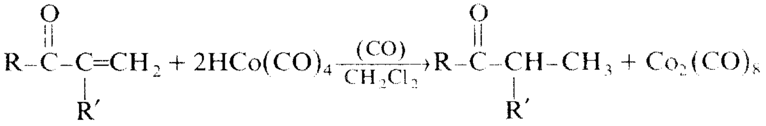
Introduction

The stoichiometric reaction of $HCo(CO)_4$ with alkenes at room conditions has been studied extensively [1]. The predominant reaction involves hydroformylation although a small amount of competitive hydrogenation also occurs [2]. On the other hand, conjugated dienes [3] and phenyl substituted ethylenes [4] are readily hydrogenated under the same conditions, frequently leading to saturated hydrocarbons exclusively. Conjugated ketones, aldehydes [5], and esters [6] undergo hydroformylation as well as hydrogenation [7].

A recent study of the mechanism of the reaction of α,β-unsaturated esters with $HCo(CO)_4$ demonstrated kinetic behavior of these substrates similar to that observed with simple alkenes [8] and both hydrogenation and hydroformylation products were observed. We wish to report that the rate expression for the reaction

0022-328X/88/$03.50

of the α,β-unsaturated ester, dimethyl itaconate involves first order dependence of $[HCo(CO)_4]$ and no aldehydic products are produced. The reactions of α,β-unsaturated ketones also leads to hydrogenated products but here the rate law involves a second order dependence on $[HCo(CO)_4]$. Both types of reaction involve the stoichiometry:



$$R-\overset{\overset{O}{\|}}{C}-\underset{\underset{R'}{|}}{C}{=}CH_2 + 2HCo(CO)_4 \xrightarrow[CH_2Cl_2]{(CO)} R-\overset{\overset{O}{\|}}{C}-\underset{\underset{R'}{|}}{C}H-CH_3 + Co_2(CO)_8$$

(for the itaconate $R' = CH_2CO_2CH_3$, $R = OCH_3$)

Results

Rate of dimethyl itaconate hydrogenation

The rate of hydrogenation of dimethyl itaconate was followed by gas chromatographic analysis and by methods previously described [4]. The reactions were performed in methylene chloride at 22 °C under flowing (one atmosphere) gas pressure. The rates observed under various conditions are reported in Table 1. At the low conversions employed for the initial rate technique, no products were observed other than dimethyl α-methylsuccinate (gas chromatography) and a high conversion run failed to show any hydroformylation product (NMR spectroscopy).

The hydrogenation reaction was found to be first order in dimethyl itaconate (DMI), first order in $HCo(CO)_4$ and inverse first order in CO:

$$\text{rate} = k_{\text{obs}}[\text{DMI}][HCo(CO)_4][CO]^{-1}$$

Initially-added $Co_2(CO)_8$ had a catalytic effect similar to that previously reported for ethyl acrylate [8]. The use of $DCo(CO)_4$ produced an inverse isotope effect, $k_H/k_D = 0.60$, similar to that previously reported for styrene derivatives [4]. A high

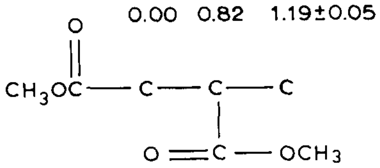
Table 1

Rate of hydrogenation of dimethyl itaconate in CH_2Cl_2 at 22 °C

$[\text{Ester}]_0$ ($\times 10^2$)	$[HCo(CO)_4]_0$ ($\times 10^2$)	$[CO]$ [a] ($\times 10^3$)	Rate ($M\ s^{-1}$) ($\times 10^7$)	k_3 (s^{-1}) [f] ($\times 10^7$)
2.84	12.68	7.20	3.08	6.16
5.35	5.61	7.20	2.48	5.95
5.68	11.1	7.20	5.09	5.81
2.84	12.86	1.2	17.9	5.90
5.68	8.74	1.5	20.0	6.03
5.68	9.23	7.0	12.0	5.5
5.68	19.9 [b]	7.20	16.4	10.45
2.84	12.68 [c]	7.20	5.05	10.1
2.37	6.29	7.20	0.233 [d]	0.562
9.44 [e]	10.57	7.20	18.0	13.0

[a] Calculated from the solubility of CO in CH_2Cl_2 [9] and $HCo(CO)_4$ dissociation [10]. [b] $DCo(CO)_4$: $k_H/k_D = 0.60 \pm 0.03$. [c] $Co_2(CO)_8 = 3.96 \times 10^{-2}$ M at beginning of reaction. [d] At 0 °C. [e] Methyl methacrylate. [f] k_3 is the experimental rate constant for hydrogenation, determined by the initial rate technique.

conversion reaction (76.4% by GLC) with $DCo(CO)_4$ gave dideuterio dimethyl α-methyl succinate with the deuterium distribution (proton NMR integration) shown below.



Partial hydrogenation reactions of DMI with $DCo(CO)_4$ were also analyzed by GC/MS for deuterium distribution. A reaction which produced 5.94% dimethyl α-methylsuccinate was found to contain 5.0% monodeutero (d_1) and 0.0% dideutero (d_2) DMI in the recovered mixture. A reaction which gave 43.6% saturated product was found to have 21.1% d_1, 3.9% d_2, and 0.0% d_3 and d_4 in the recovered DMI. Although the saturated product yielded a molecular ion peak in the mass spectrometer which was too small to use for quantitative deuterium distribution determination, the major fragment peak group at $m/z = 128$–133 (dimethyl α-methylsuccinate minus methoxy) indicated mainly d_2 ($m/z = 131$), with small amounts of d_0, d_1, d_3, and d_4, and with species greater than $d_4 = 0.0\%$.

Rate of methyl vinyl ketone hydrogenation

The rate of hydrogenation of 3-buten-2-one (methyl vinyl ketone) was measured as above for dimethyl itaconate, except that the reaction was performed in pentane at 0 °C. The rates as a function of several variables are reported in Table 2.

The hydrogenation reaction was found to yield a rate expression similar to that for the ester (above), except that it is second order in $HCo(CO)_4$:

$$\text{rate} = k_{\text{obs}}[\text{MVK}][HCo(CO)_4]^2[CO]^{-1}$$

As with the ester, the reaction is catalyzed by $Co_2(CO)_8$, but has a much less pronounced inverse isotope effect ($k_H/k_D = 0.86 \pm 0.03$).

Table 2

Rate of hydrogenation of methyl vinyl ketone in pentane at 0 °C

$[\text{Ketone}]_0$ $(\times 10^2)$	$[HCo(CO)_4]_0$ $(\times 10^2)$	$[CO]$ [a] $(\times 10^2)$	Rate ($M\ s^{-1}$) $(\times 10^6)$	k_4 (M^{-1}) [f] $(\times 10^4)$
5.90	6.60	1.04	9.53	3.90
11.8	6.90	1.04	22.2	4.11
11.8	13.8	1.04	87.9	4.07
11.8	6.45	0.25	84.3	3.96
11.8	5.75	1.04	62.9 [b]	16.7
11.8	6.59	1.04	35.0 [c]	67.6
11.8	7.70 [d]	1.04	32.4	4.45
11.8	6.10 [e]	1.04	92.7	21.9

[a] Calculated from the solubility of CO in pentane [9] and $HCo(CO)_4$ dissociation [10]. [b] At 11.0 °C. [c] At 20.5 °C. [d] $DCo(CO)_4$; $k_H/k_D = 0.86 \pm 0.03$. [e] Initial concentration of $Co_2(CO)_8 = 4.09 \times 10^{-2}$; $k_4 = 4.01 \times 10^{-4}$, including total Co as $Co_2(CO)_8 + HCo(CO)_4$. [f] k_4 is the experimental rate constant for hydrogenation, determined by the initial rate technique.

Table 3

Rate of hydrogenation of phenyl vinyl ketone (PVK), 2-methylene-1-indanone (MI), and 1,3-diphenyl-3-buten-2-one (DPB) in CH_2Cl_2 at 0 °C

$[\text{Ketone}]_0$ $(\times 10^2)$	$[HCo(CO)_4]_0$ $(\times 10^2)$	$[CO]$ [a] $(\times 10^3)$	Rate $(M\ s^{-1})$ $(\times 10^6)$	k_4 (M^{-1}) [f] $(\times 10^3)$
PVK				
3.00	3.97	7.20	8.24	1.25
3.00	8.82	7.20	34.6	1.07
1.50	2.26	7.20	1.34	1.26
3.00	2.16	7.20	2.21	1.14
3.00	4.11	1.2	51.1	1.21
3.00	3.7 [b]	7.20	7.52	1.32
3.00	4.26 [c]	7.20	17.6	2.33
3.00	4.26 [d]	7.20	48.9	6.47
3.00	3.84 [e]	7.20	21.4	3.48
MI				
3.61	4.51	7.20	8.34	0.818
1.80	4.51	7.20	4.22	0.828
3.61	1.97	7.20	1.91	0.98
DPB				
2.03	4.47	7.20	21.9	3.89
2.03	2.23	7.20	5.67	3.76

[a] Concentration calculated from the solubility of CO in CH_2Cl_2 [9] and the dissociation of $HCo(CO)_4$ [10]. [b] $DCo(CO)_4$; $k_H/k_D = 0.90 \pm 0.03$. [c] At 10.5 °C. [d] At 20.0 °C. [e] Initial concentration of $Co_2(CO)_8 = 1.41 \times 10^{-2}$ M; $k_4 = 1.16 \times 10^{-3}$, including total Co as $Co_2(CO)_8 + HCo(CO)_4$. [f] k_4 is the experimental rate constant for hydrogenation, determined by the initial rate technique.

Rate of phenyl vinyl ketone hydrogenation

The rate data for the stoichiometric hydrogenation of phenyl vinyl ketone in methylene chloride at 0 °C under various conditions is shown in Table 3. The rate law is the same as for methyl vinyl ketone; a similar isotope effect (0.90 ± 0.03) and catalysis by $Co_2(CO)_8$ are also observed. Also shown in Table 3 are the rates for the related compounds 2-methylene-1-indanone and 1,3-diphenyl-3-butene-2-one.

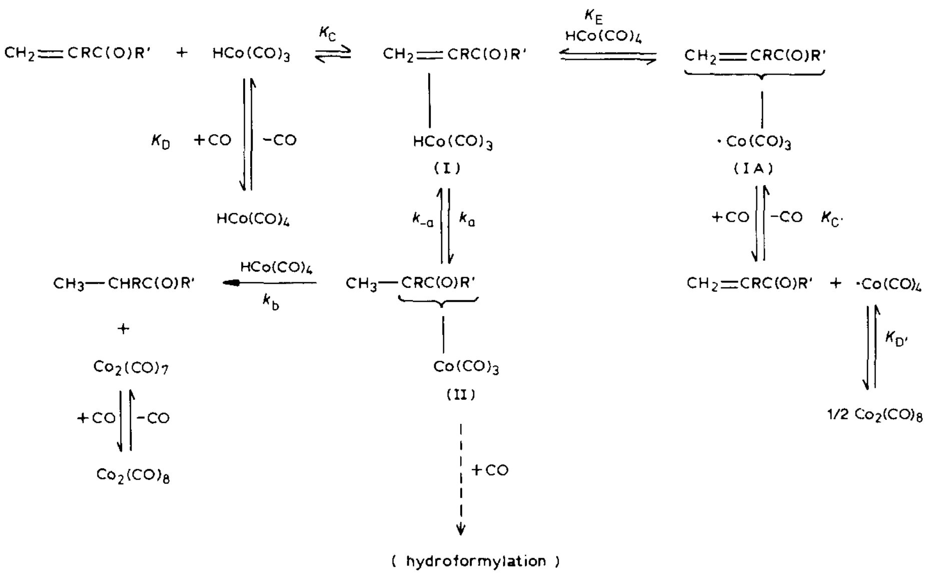
Phenyl vinyl ketone and 2-methylene-1-indanone undergo faster hydrogenation than methyl vinyl ketone, but only by a factor of three and two, respectively; the rate for 1,3-diphenyl-3-butene-2-one (diphenyl methyl vinyl ketone), however, was about ten times faster.

Discussion

The kinetic effects on the hydrogenation reaction of dimethyl itaconate were found to be very similar to those recently reported for ethyl acrylate, except that no hydroformylation was observed under the reaction conditions employed. While the rate and extent of CO absorption were not monitored in this study, no aldehyde products were observed (gas chromatography, proton NMR spectroscopy). The rate expression previously reported [8] reduces to that observed here:

$$\text{rate} = k_{\text{obs}}[\text{ester}][HCo(CO)_4][CO]^{-1}$$

where the observed rate constant may include equilibrium constants and specific



Scheme 1. Hydrogenation scheme.

rate constants which occur prior to the slow step. The mechanism is compatible with the currently reported data and the previously proposed [8] mechanism (see Scheme 1).

The exchange of DMI indicates that the formation of complexes I and II are reversible, and that this process (k_{-a} and K_C or k_{-a}, K_E, $K_{C'}$) must be similar in rate to the second addition step of the hydrogenation (k_b). The formation of a π-allylic complex (instead of complex II) would seem to be precluded by the lack of appreciable isomerization and the small amount of d_3 and d_4 in the hydrogenation product.

The failure to observe any aldehyde from the reaction of DMI with $HCo(CO)_4$, in contrast to the reported [8] behavior of simple acrylates, may be rationalized by the larger steric requirements for CO migratory insertion into the precursor alkyl species [11].

The rate expression and $Co_2(CO)_8$ catalysis for the α,β-unsaturated ketones are similar to the esters except for the second order dependence in $HCo(CO)_4$, indicating a change in the slow step to k_b. The faster overall reaction of the ketones (compared to the ester) supports this conclusion.

The hydrogenation scheme (Scheme 1) incorporates the feature of catalysis of $Co_2(CO)_8$, based upon previously studied steps, such as $K_{D'}$ [3c]. However, the exchange equilibrium K_E between complex IA and $HCo(CO)_4$ must be fast, in order for this scheme to hold [8]. The formation of complex I, by the forward steps of both K_C and K_E, is analogous to that for the similar complexes formed by alkenes and dienes. Complex II could exist in several possibly interconvertible forms: as a σ complex at the α-carbonyl position, analogous to alkenes [1]; as a radical pair, analogous to that formed with phenylalkenes [4], (the failure to see CIDNP emission spectra does not necessarily rule out this structure); or what is most attractive to us, as an oxapropenyl π-complex (pseudo π-allyl) [5,6]. The faster overall rate of hydrogenation for the ketones (vs. esters) supports the π-complex interpretation for complex II; the better conjugation between the carbonyl and vinyl groups in ketones [12] would result in greater stability for the delocalized π-complex and an increase in rate in k_a, such that $k_a > k_b$.

The rate differences observed among the ketones is relatively small, although the two phenyl groups of 1,3-diphenyl-3-buten-2-one result in a ten-fold rate enhancement compared to methyl vinyl ketone. This may indicate again the assistance due to additional conjugation.

Experimental

Materials

$HCo(CO)_4$ and $DCo(CO)_4$ [4] were prepared in CH_2Cl_2 or pentane immediately before use by methods previously described [4]. These were usually pale yellow in color at the initial time of use in a reaction. Solvents were dried and then saturated with CO during the $HCo(CO)_4$ preparation. Pentane was used as a solvent for MVK reactions because of the similarity to solvents employed in previous reports [3,4,8] and for convenience in gas chromatography. Dimethyl itaconate was purchased from Aldrich Chemical Co. and was found to be 97.2% pure as received. It was used without further purification because the main impurity was dimethyl mesaconate which reacts much more slowly than dimethyl itaconate. Methyl vinyl ketone was also purchased from Aldrich Chemical Co. (99%) and used without further purification. Phenyl vinyl ketone, 2-methylidene 1-indanone, and 1,3-diphenyl-3-buten-2-one were prepared by the Mannich condensation of the appropriate ketone with formaldehyde, followed by steam distillation and column chromatography through alumina, from which they were eluted with petroleum ether and toluene [13]. The purities obtained were 95, 97, and 98% respectively; the impurities were mainly the original ketones.

General techniques

Gas chromatography was performed with a Hewlett–Packard Model 5890A equipped with a Hewlett–Packard Model 3390A reporting integrator using a 25 m × 0.53 mm capillary column coated with phenyl methyl silicone. NMR spectra were recorded on a Varian Associates EM 360 spectrometer at 60 MHz and 14,000 G; tuned with an external standard using Me_4Si(TMS). Mass spectra were obtained employing a Hewlett–Packard Model 59970 MSD equipped with a Model 5970B gas chromatograph inlet. The GC/MS spectra were obtained at a 70 eV ionizing voltage and mass resolution was achieved by the quadrupole method.

Kinetic experiments were performed as previously described [4] under a positive pressure of CO or an inert gas. Solutions of $HCo(CO)_4$ were standardized by quenching with excess 1,1-diphenylethylene immediately before each kinetic run [4a]. Experiments were initiated by adding the unsaturated compound to the rapidly stirred $HCo(CO)_4$ solution which had been previously saturated with CO or N_2 and thermostated ($\pm 0.1°$C). To secure partial atmospheres of CO, the CO and N_2 were premixed in a vacuum storage flask (0.5 l) to a total pressure of 800 torr. This flask was then attached to the small (15 ml) reaction flask by a ground joint and the apparatus vented with the excess gas pressure. Reagents were then introduced via syringe and the experiments performed as before, but under static gas pressure.

Aliquots were periodically removed at low $HCo(CO)_4$ conversions (1–5%) and quenched with an excess (10-fold) of 2,6-dimethylpyridine [14]. Typically, the quenched mixtures were allowed to stand for several hours, the $Co_2(CO)_8$ was then frozen out at −78 °C and the yellow-brown solutions were then analyzed by gas chromatography. Some kinetic runs were performed in CO flushed NMR sample tubes and spectra were recorded continuously as the sample warmed from −78 °C.

Deuterium distribution experiments with dimethyl itaconate and $DCo(CO)_4$ were performed in conjunction with the isotope effect experiments. In addition to measuring the quenched rate point samples, the remaining reaction solution was allowed to go to completion. The final percent reaction was measured by gas chromatography, as with quenched samples. The solution was cooled with dry ice/isopropanol, filtered through glass wool, refiltered through a C_{18} Sep-Pak cartridge (Waters Assoc.), evaporated at 25 °C to an oil, and then taken up in $CDCl_3$ for NMR spectrum recording and integration. Deuterium content was determined by integration difference from the proton spectra of pure standards. Samples for GC/MS were prepared in a similar manner. After reaction, filtration and evaporation, mixtures were taken up in CH_2Cl_2. One micro-liter portions of these 10% solutions were injected by an automatic liquid sampler (ALS) into the GC/MS. Quadrupole spectra of each gas chromatograph peak were automatically stored in a computer workstation. Digital relative abundance, as well as bar graph spectra, were then reported by the printer/plotter. Deuterium species were then calculated by correcting for neighboring peaks by an iterative procedure based upon the all-hydrogen standard spectra.

Registry numbers

$HCo(CO)_4$, 16842-03-8; dimethyl itaconate (dimethyl 2-methylenebutanedioate), 617-52-7; 2-methylene-1-indanone 13261-70-6; methyl vinyl ketone (3-buten-2-one), 78-94-4; phenyl vinyl ketone (1-phenyl-2-propen-1-one, 768-03-6; 1,3-diphenyl-3-buten-2-one, 68646-49-1; methyl methacrylate, 80-62-6.

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